Physics 131
General Physics I
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Summary--Statistical Physics
Unit 13

Statistical physics allows us to find the governing rules for person-sized systems (rules that relate such observable properties as energy, pressure, temperature) from studying the likelihood of different configurations of individual atoms. We began with the notions of microstates and macrostates. A microstate completely describes a system--it gives the complete set of quantum numbers for each atom. Macrostates describe a system in terms of the large-scale observable properties such as pressure and temperature. As a result, a single macrostate could equally well describe many different microstates. The basis for statistical physics is the notion that all quantum microstates are equally likely, if they are energetically allowed (i.e. within the constraints of conservation of energy, known in this context as the first law of thermodynamics). Given the equal probability of microstates, the macrostate (as defined by some macroscopically observable property, like total energy) that is most likely is the one representing the greatest number of microstates. Because this is a probability argument, there is some statistical fluctuations, just as flipping a coin ten times does not always yield 5 heads. The relative variation of large-scale properties of a macrostate is roughly like one over the square root of the number of atoms, which produces very well defined properties for typical macroscopic samples with 10^{20} or more atoms.

For a binary system, where each of N particles has one of two possible states, if n of them choose the first possibility, then the number of microstates is given by

$$\#\,microstates = \frac{N!}{(N-n)!\,n!}\,.$$

This produces very large numbers, numbers that are beyond the capability of our calculators, so we take the logarithm of this value and define that to be the entropy S:

$$S = k_B \ln(\#\,microstates),\ \ where$$

$$k_B = 1.38\times 10^{-23}\ {}^{J}\!/_{K}$$

which we can evaluate with the help of the Stirling approximation

$$\ln(N!) \approx \tfrac{1}{2}\ln(2\pi) + (N+\tfrac{1}{2})\ln(N) - N\,.$$

An additional reason to choose this definition of entropy is that the entropy of a system made up of two systems was the sum of the entropies of the individual systems. If energy can flow between these two systems, it does so until the combined entropy reaches a maximum (i.e. the maximum number of microstates). This occurs when the derivative of the total (combined) entropy with respect to energy flow goes to zero, like maximizing any function. This implies that the quantity

$$\frac{dS}{dE} \equiv \frac{1}{T}$$

must be the same for each system. This implicitly defines the temperature T, and agrees with the notion that heat flows from one system to another until they reach the same

temperature. The notion of entropy always increasing is referred to as the second law of thermodynamics.

We also found that for a single particle in thermal equilibrium with its surroundings at temperature T, the ratio of the probability of being in one quantum state versus another depended on the energy difference between the two states as given by the Boltzmann factor:

$$\frac{\text{Probability 1}}{\text{Probability 2}} = e^{\Delta\varepsilon/k_B} .$$

This factor always makes the lower energy state more probable. We then found, if we know all of the quantum states that are [reasonably] accessible to a quantum particle, the absolute probability (as opposed to relative probability expressed above by the Boltzmann factor) of finding the particle in a particular state is given by

$$\text{Prob}(\varepsilon) = \frac{e^{-\varepsilon/k_B T}}{Z} \text{ where } Z = \sum_{\text{all states}} e^{-\varepsilon/k_B T} .$$

This latter term, the sum Z, is called the partition function, and is the scaling factor that makes the sum of all the probabilities come out to equal one.

We can use the probability expression above to find average values of various properties. Certainly the most useful of these is the average energy, which for a single particle is given by the sum of the energy of each possible state times the probability of that state, or

$$E_{average} = \frac{\sum \varepsilon\, e^{-\varepsilon/k_B T}}{Z} .$$

We used this expression on the particle in a box wave functions to find the energy of N particles confined to a box:

$$E_{total} = \frac{3Nk_B T}{2} .$$

This expression is very useful for ideal gases, which behave very much according to our quantum particle in a box model. We finally connected this quantum energy with the macroscopic energy that we experience as associated with forces and work, and found the ideal gas law:

$$PV = Nk_B T$$

which we subsequently verified experimentally, and in the process, found the value for absolute zero of -273° C.